2010 INTERNATIONAL WORKSHOP ON ENVIRONMENT AND ENERGY

San Diego, California November 2 - 4, 2010

Synthesis and characterization of functional nanocontainers for active corrosion protection

João Tedim

University of Aveiro, Portugal

SECoP Surface Engineering and Corrosion Protection

university of aveiro
theoria poiesis praxis

ciceco
centre for research in ceramics & composite materials

1. Introduction

Direct incorporation of corrosion inhibitors in coating formulations can lead to several problems:

-**detrimental interaction** between inhibitors and coating matrix (**technical**)

-**constant/spontaneous leaching** of inhibitors into the environment (**environmental and economical**)

Limitation of the coating protective action in time and magnitude

Nanocontainer

Corrosion inhibitor

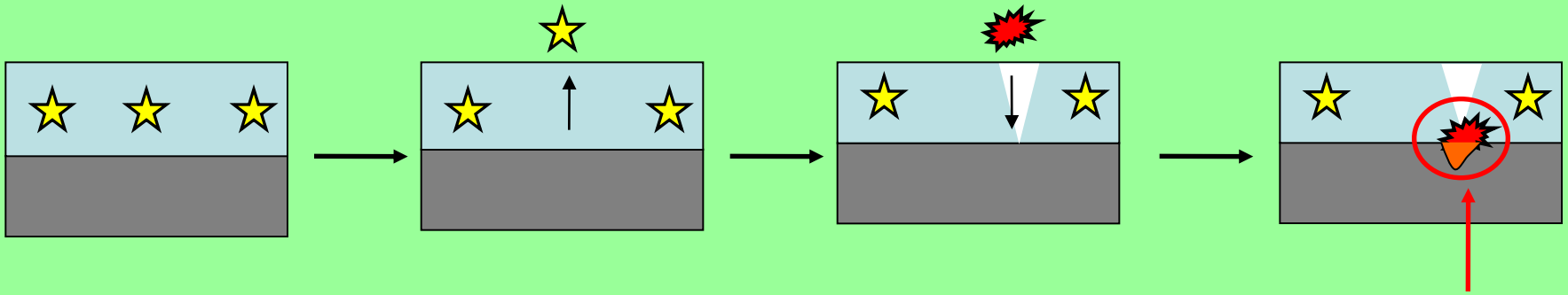
Coating

Metallic substrate

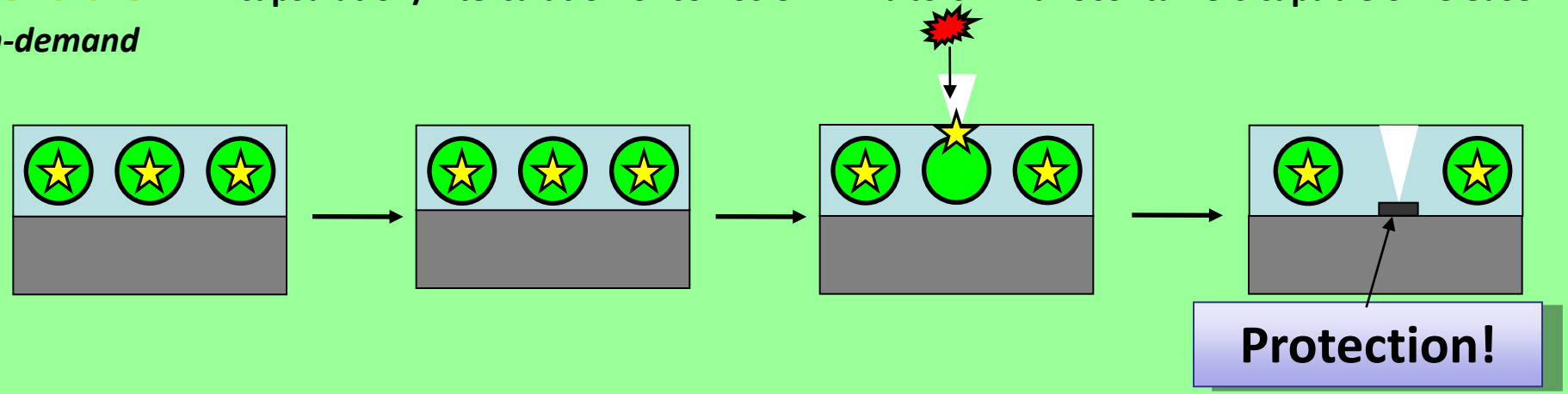
Aggressive species

Corrosion products

Protective film



Solution Encapsulation/intercalation of corrosion inhibitors in nanocontainers capable of *release-on-demand*



Micro/nanocontainer + Corrosion inhibitor >= Chromates

Inert, hosting structures

Release mechanisms

Active protection

Low toxicity

Types of containers:

-inorganic, organic, hybrid

Release mechanisms:

-mechanical impact

-pH -H_2O

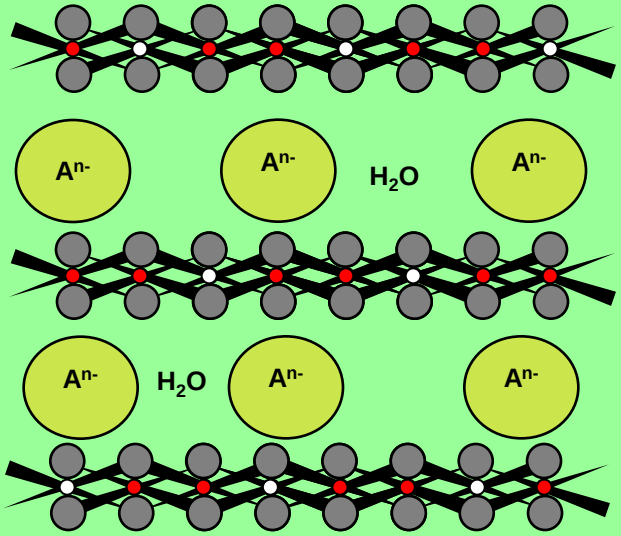
-presence of aggressive species (e.g. chlorides)

Potential advantages related to this strategy:

- improvement of coating integrity
- smaller amounts of inhibitor required
- development of new value-added products
- comply with environmental law regulations

Layered double hydroxides (LDHs)

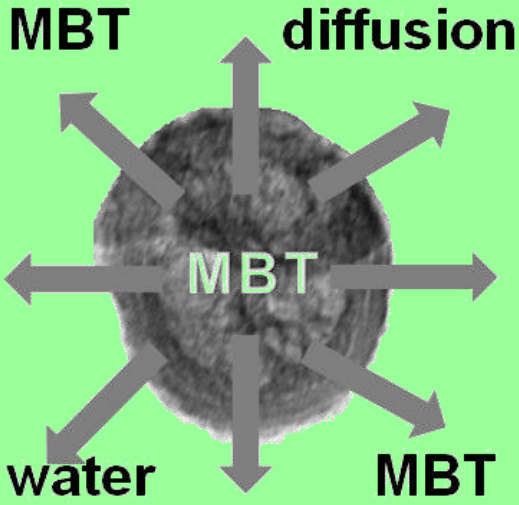
$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]A^{n-}_{x/n}\cdot mH_2O$



Applications:

Sorbents, Drug-delivery systems, Polymer stabilizers, Heterogeneous catalysis

Silica nanocapsules (SiO_2)



Applications:

Drug-delivery systems

Transport carriers

Nano-reactors

2. Experimental

- **Synthesis of LDHs**

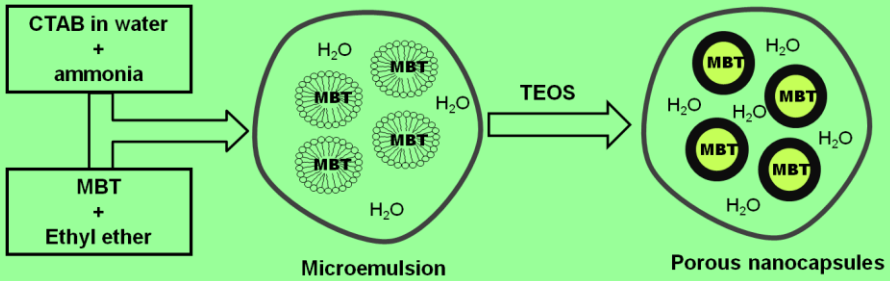
-methodologies applied: ion-exchange, calcination-rehydration

-corrosion inhibitors intercalated: MoO_4^{2-}, VO_3^-, MBT

- **Synthesis of SiO_2**

-oil-in-water microemulsion

-corrosion inhibitor: MBT



- **Structural/morphological characterization**

XRD, SEM, TEM

- **Release studies**

HLPC

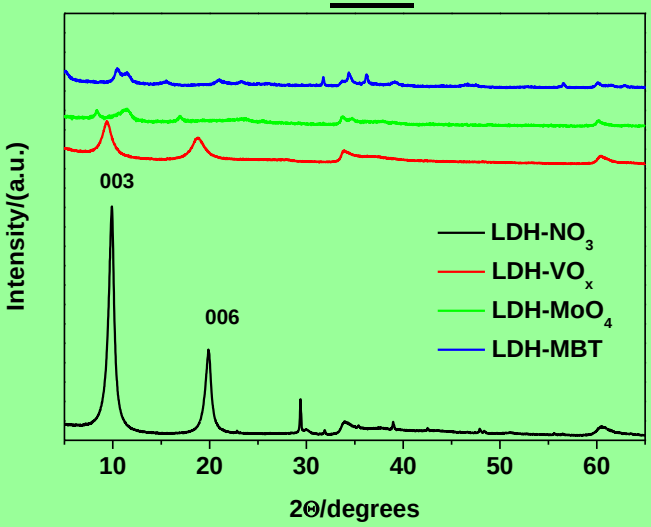
- **Corrosion studies**

EIS

3. Struture and morphology

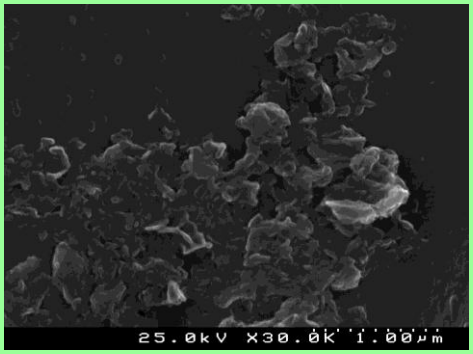
LDHs

XRD

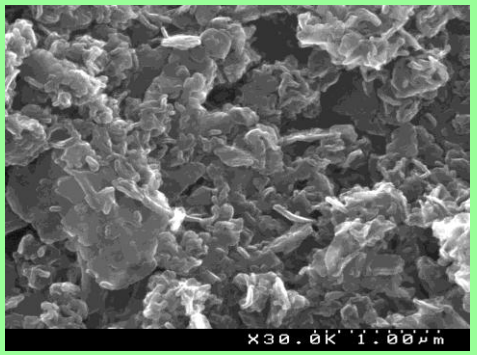


- Peak positions at low angles: information on the gallery height (anion size and orientation)

SEM

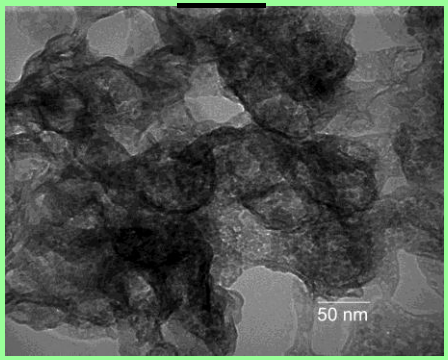


LDH-NO_3



LDH-VO_x

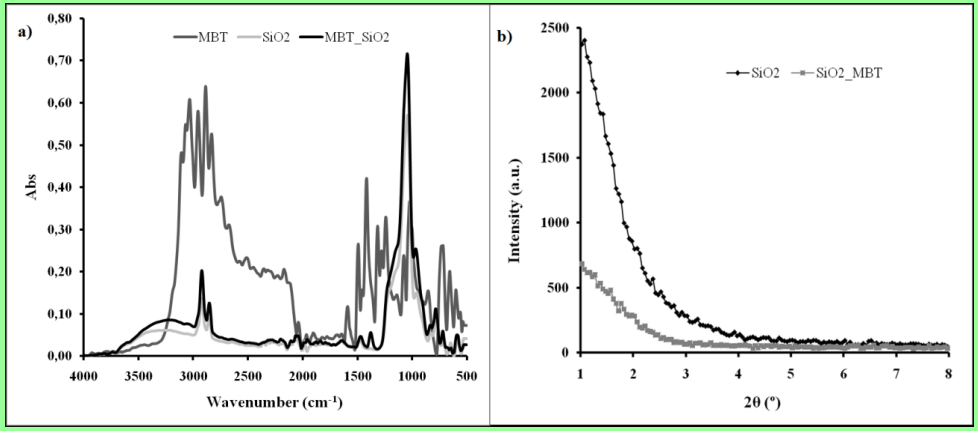
TEM



- Plate-like morphology
- LDH particles: 200-400 nm diameter and 20-40 nm height

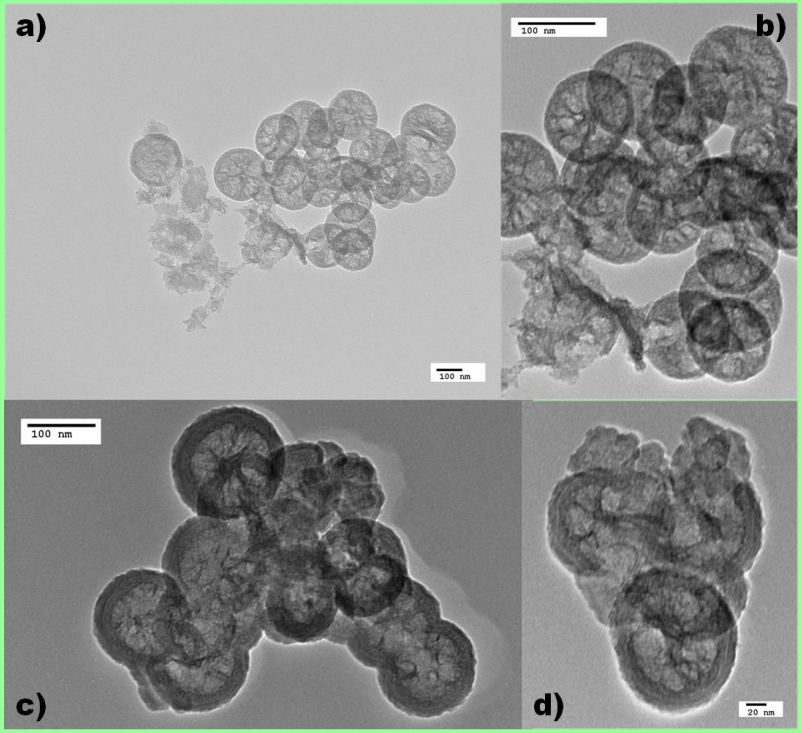
SiO_2

FTIR

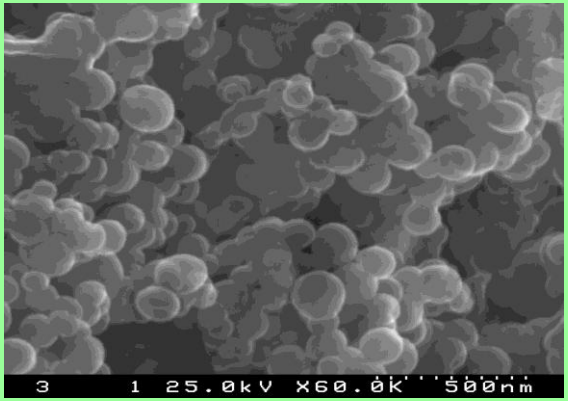


XRD

TEM

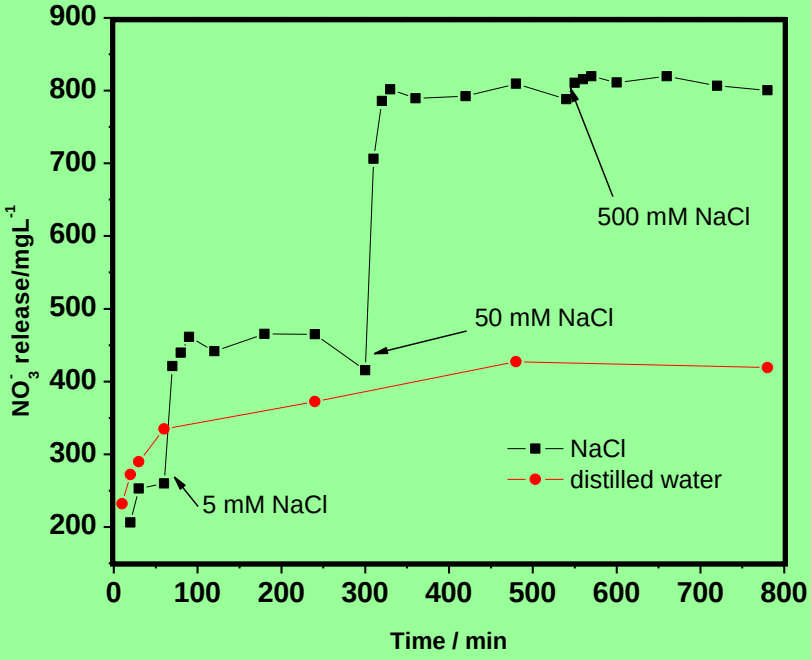


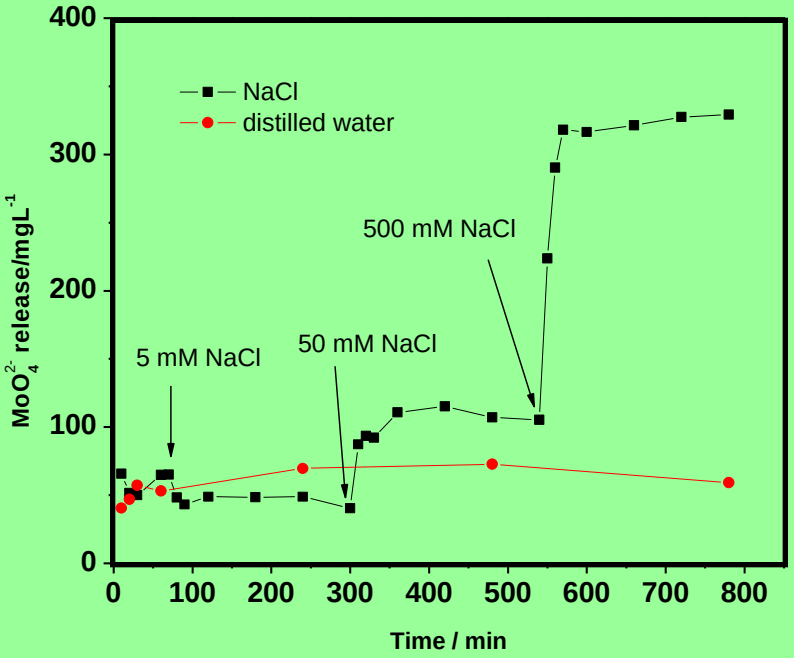
SEM



- **Porous, spherical particles 150 nm diameter**
- **Different core/shell porosities**

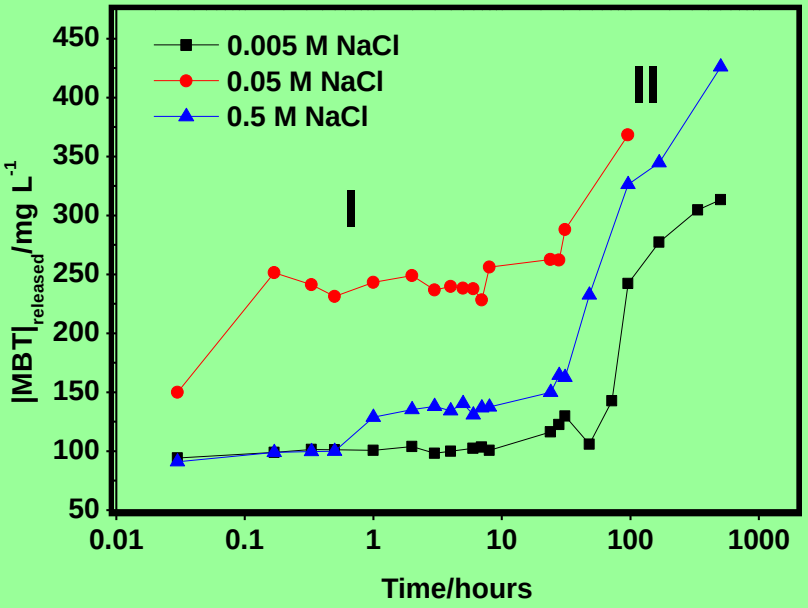
4. Release studies-LDHs



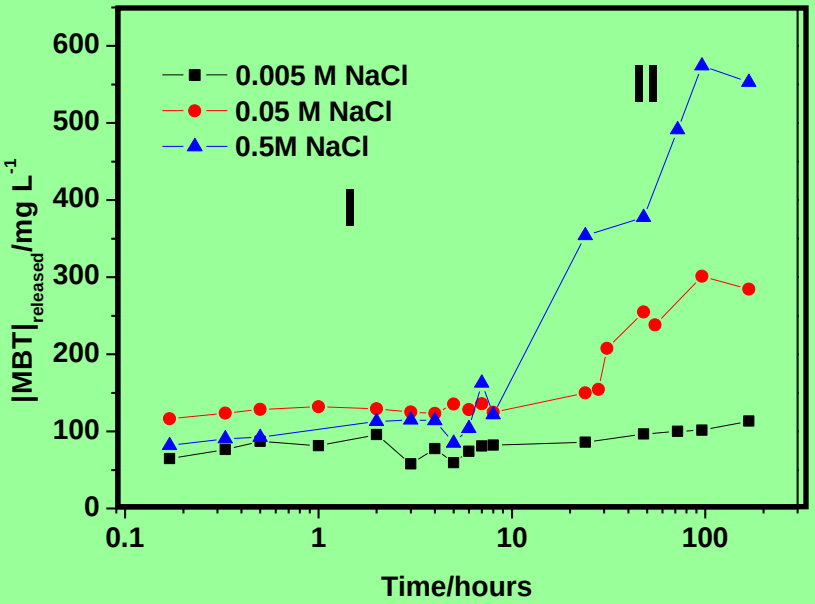


- **The release of NO_3^- and MoO_4^{2-} anions is triggered by the presence of chloride anions**

SH-MBT

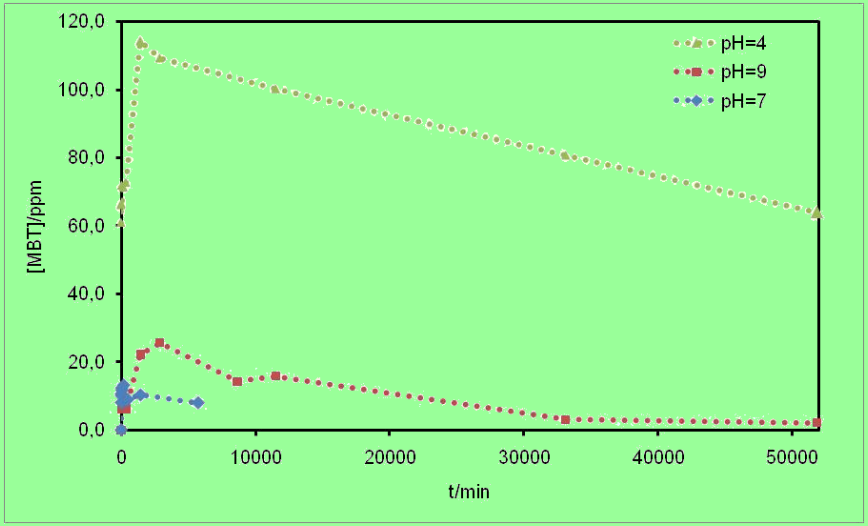


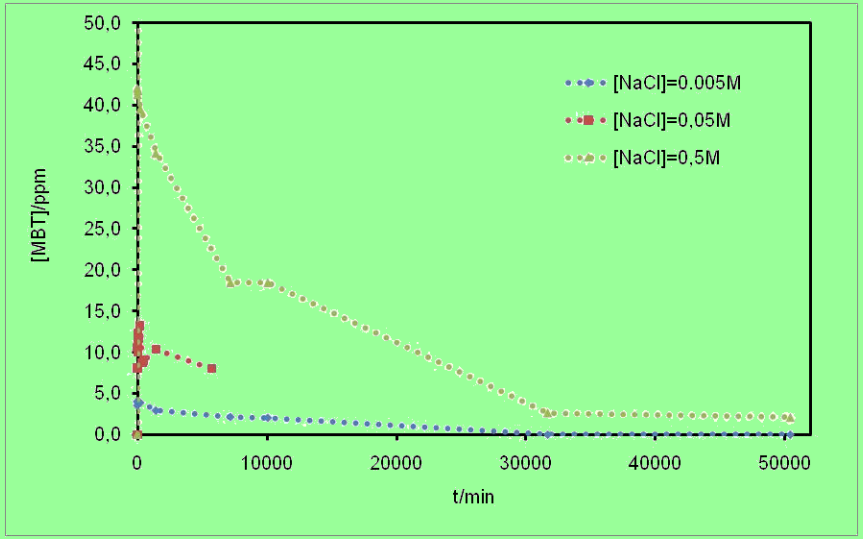
Zn(2)-Al-MBT



- **Two release profiles are observed: short (1-2h) and long timescales (>100 h)**
- **Profile at short timescales is not sensitive to the concentration of Cl^-**

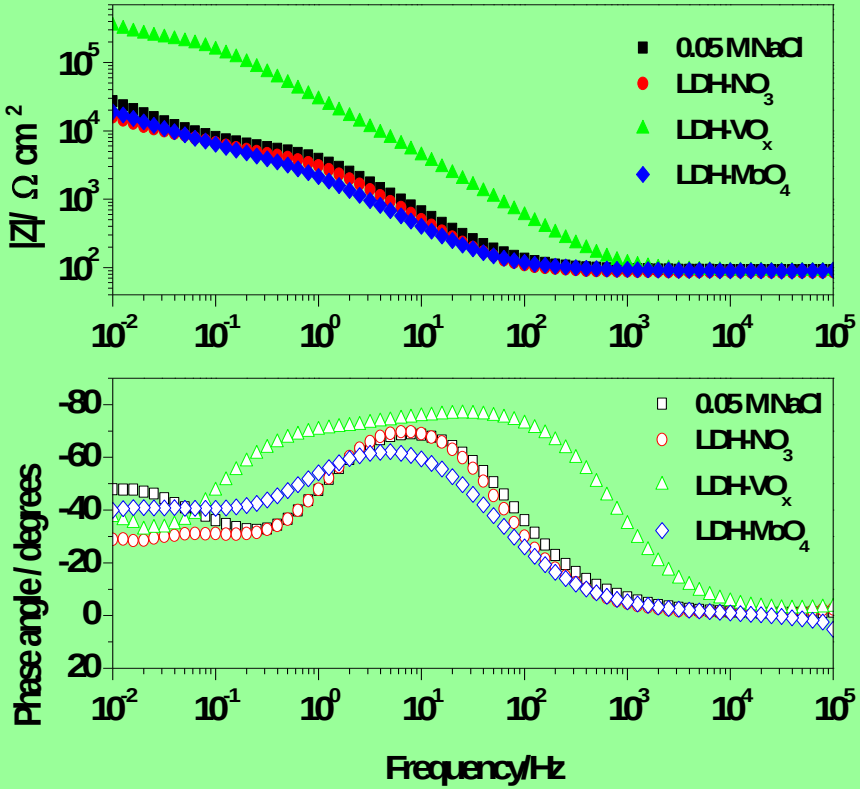
4. Release studies-SiO_2

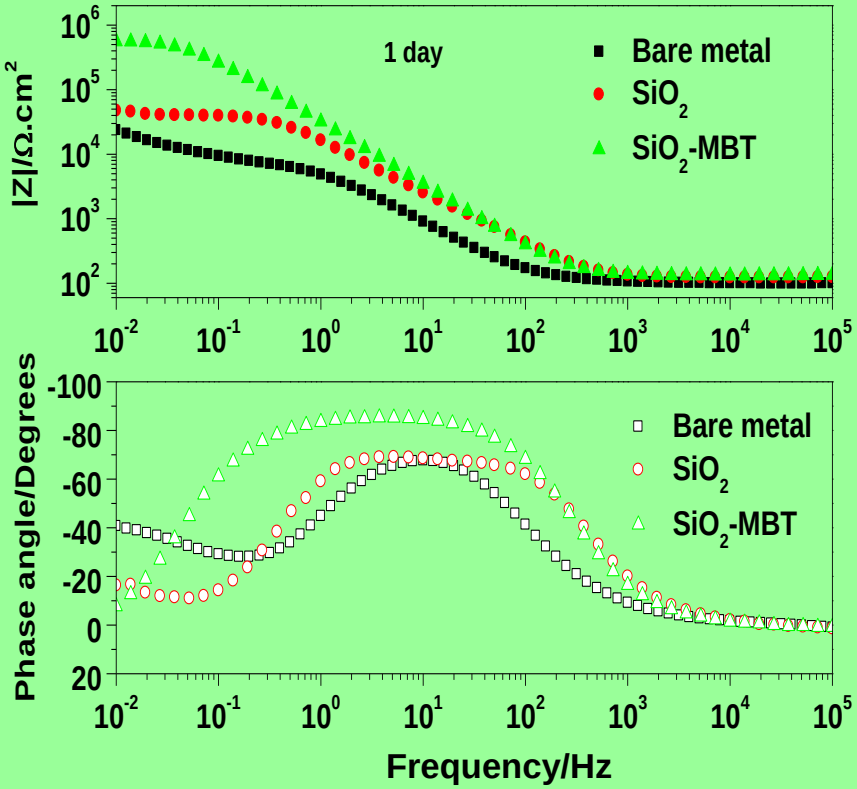




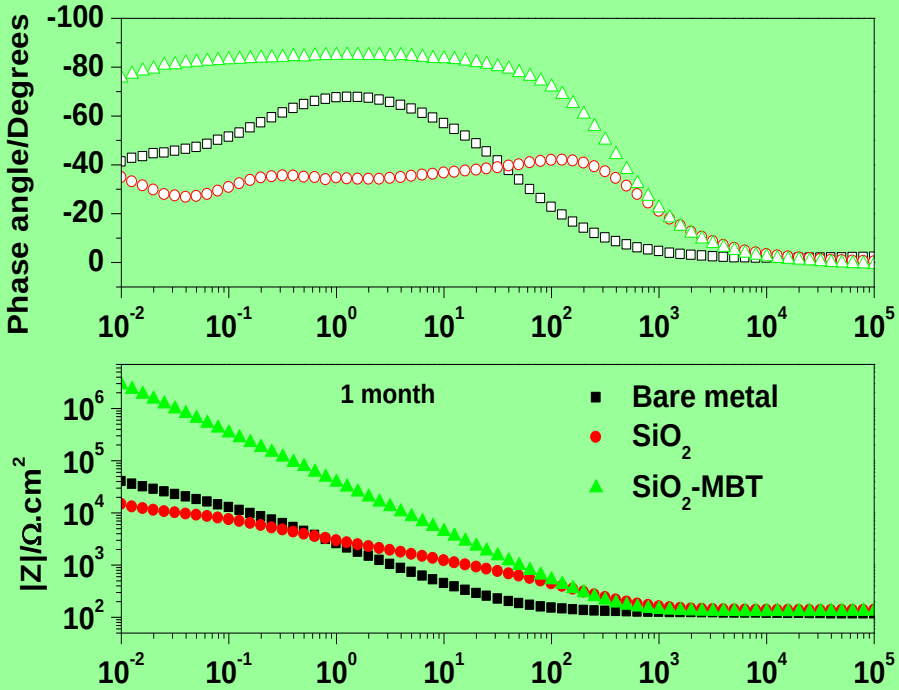
- **MBT released preferentially in concentrated NaCl solutions and acidic conditions**

5. Assessment of anticorrosion performance-EIS

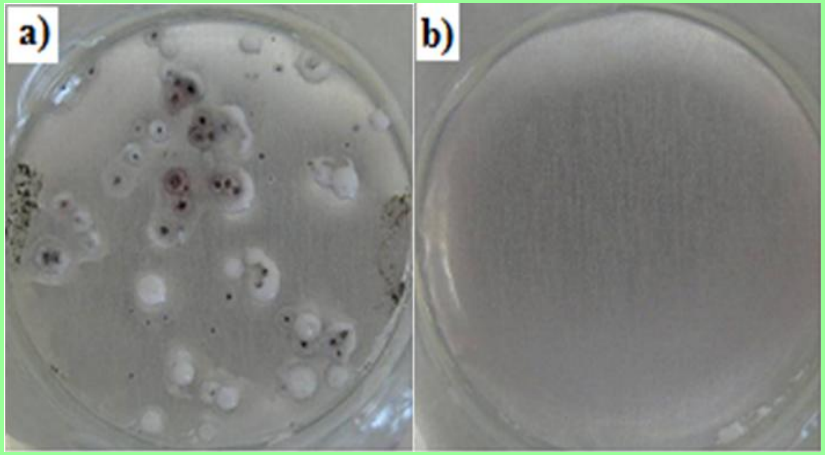




- **EIS spectra for bare AA2024 after 1 day of immersion in 0.05 M NaCl**



SiO_2 **SiO_2-MBT**



1 month of immersion in 0.05 M NaCl

- **The presence of inhibitor determines the (active) protection of the metal substrate**

Concluding Remarks

- LDH nanocontainers and SiO_2 nanocapsules were synthesized and corrosion inhibitors successfully intercalated/ encapsulated
- Release studies showed that the optimal conditions for the release of corrosion inhibitors are

  -LDHs (NaCl) -SiO_2 (pH and NaCl)
- The anticorrosion activity in solution depends on the strength of the inhibitor

Future perspectives

- Incorporation of corrosion inhibitor/nanocontainer 'pigments' in coating formulations from aeronautical, automotive and maritime industry

  -dispersion optimization via surface modification

  -assessment of the protection performance of the coatings

- Optimization of the nanocontainers for specific applications

  -action on the release response

  -screening of inhibitors, combination of inhibitors displaying synergistic effects

Acknowledgments

- Miss Alena Kuznetsova
- Mr Frederico Maia
- Dr Andrei Salak
- Dr Mikhail Zheludkevich
- Prof Mário G. S. Ferreira

European project MUST ref. NMP3-LA-2008-214261